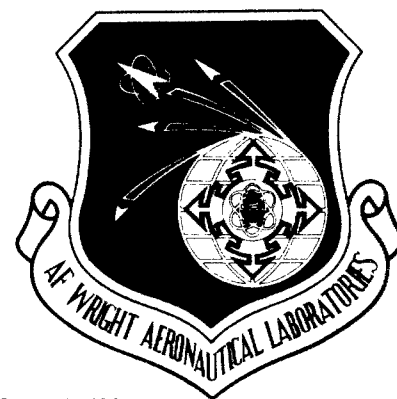AFWAL-TR-88-4197

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SYNTHESIS AND THERMAL PROPERTIES OF ARYL AND ARYLOXYETHYNYL MONOMERS FOR THERMOSET RESINS OF REDUCED CROSSLINK DENSITY

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Final Report for Period May 1982 to October 1984

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
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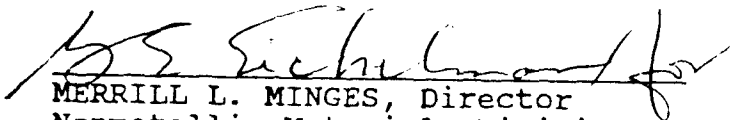This technical report has been reviewed and is approved for publication.

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A series of thermoset matrix materials with phenylethynyl and phenoxyphenylethynyl end groups were prepared to assess the extent of crosslinking in the cured resins by thermo-analytical and thermomechanical methods. These novel materials with varying flexibility and thermal stability of both the end group and backbone were evaluated against a group of materials (AT systems) known to contain a substantial number of primary acetylenic thermal crosslinking sites.

The evaluation indicated the increased thermooxidative stability of the secondary acetylenic materials over the AT systems at or below 600°F (312°C). However, above 600°F the reverse observation was true since the phenyl pendant of the secondary termini was thermally decomposed near 400°C (752°F) as measured by MS/TGA under vacuum. Cure exotherms (T_{poly}) for the monomers exhibited typical Gaussian behavior with discernable cure onsets and maxima. The approximate cure maximum for the secondary acetylene was 400°C as measured by DSC($\Delta T=20°C/min$). Percentages of weight retained varied from 64% to 92% after isothermal

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19. aging at 600°F for 200 hours in circulating air. T_g's (cured) more closely approximated the values observed for linear homopolymers.

One of the phenoxyphenylethynyl monomers with a biquinoxaline backbone was cured and its toughness was measured by fracture analysis. The results indicated a 20% increase over the room temperature value of the observed K_Q for its comparable AT analog, BA-DAB-BA.

FOREWORD

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SECTION I

INTRODUCTION

Previous Air Force research interests have emphasized the improvement of state-of-the-art thermoset matrix materials over the currently used epoxy resins in traditional structural composite applications. The incorporation of the primary acetylene as a thermally reactive end group on the backbones of thermally and thermooxidatively stable monomers (AT systems) has been well reported (Reference 1). The advantages of the use of the reactive primary acetylene end group include no generation of volatiles during cure so that voids in the matrix are eliminated. In addition, reduced absorption of water by the cured matrix under high humidity conditions allows the retention of desired mechanical properties with a resulting improvement over the 135°C service ceiling of the epoxy resins (Reference 2).

Much less attention has focused on the use of secondary acetylenes such as phenylethynyl and phenoxyphenylethynyl as the reactive end groups of a thermally stable backbone. Previous studies have centered on phenylethynyl pendants incorporated into high molecular weight polymers which undergo cure either intramolecularly or intermolecularly to form a highly fused or more lightly crosslinked polymer respectively. Pendants that react intramolecularly polymerize near 250°C max as indicated by differential

scanning calorimetry (DSC, ΔT=20°C/min) (References 3-5).
However, when the phenylethynyl group was randomly spaced
along the polymer backbone, the thermally induced
intermolecular crosslinking reaction occurred at 430-450°C
by DSC (ΔT=20°C/min) (Reference 6). This 200°C difference
in cure exotherm is presumed to occur because of the
dependence of additional energy input to move the reactive
end groups into position to undergo the crosslinking
reaction. An aromatic imide oligomer with terminal
phenylethynyl groups was recently reported to have a very
broad onset of polymerization beginning at 250°C and
maximizing at 420°C (DSC, ΔT=20°C/min) (Reference 7).

This report describes the preparation and thermo-
analytical characterization of monomers with aryl and
aryloxyethynyl terminal end groups. A direct comparison of
the thermooxidative stability of resins produced from these
analogs was made with the corresponding AT systems. This
report also addresses the concept of reducing the crosslink
density via the incorporation of secondary acetylenic
reactive end groups into the monomers thus providing a
means to improve the toughness of the cured resin without
the addition of oligomeric products (Reference 8).

SECTION II

RESULTS AND DISCUSSION

1. Syntheses of Phenylethynyl Substituted Monomers With Phenylene R (Reference 9) and Imide Moities in the Backbone

a. Phenylene R bisbenzenes 1 and 2

The secondary acetylene substituted monomers, 1,3-bis-(3-phenylethynylphenoxy)benzene (1) and 4,4'bis(3-phenyl-ethynylphenoxy)diphenylsulfone (2) were prepared in 60-64% yield by a nucleophilic displacement reaction using phenylacetylene with a previously reported copper and organopalladium catalyst system upon 1,3-bis(3-bromophen-oxy)benzene and 4,4'-bis(3-bromophenoxy)diphenylsulfone (Reference 10).

$$Br - R - Br \ + \ HC \equiv C\phi$$

$$\phi_3 P, \ CuI$$
$$(\phi_3 P)_2 \ PdCl_2 \qquad \bigg\downarrow \qquad \begin{array}{c} Et_3N \\ reflux \end{array}$$

$$\phi C \equiv C - R - C \equiv C\phi$$

R = ⬡—O—⬡—O—⬡ **MONOMER (1)**

⬡—O—⬡—SO₂—⬡—O—⬡ **MONOMER (2)**
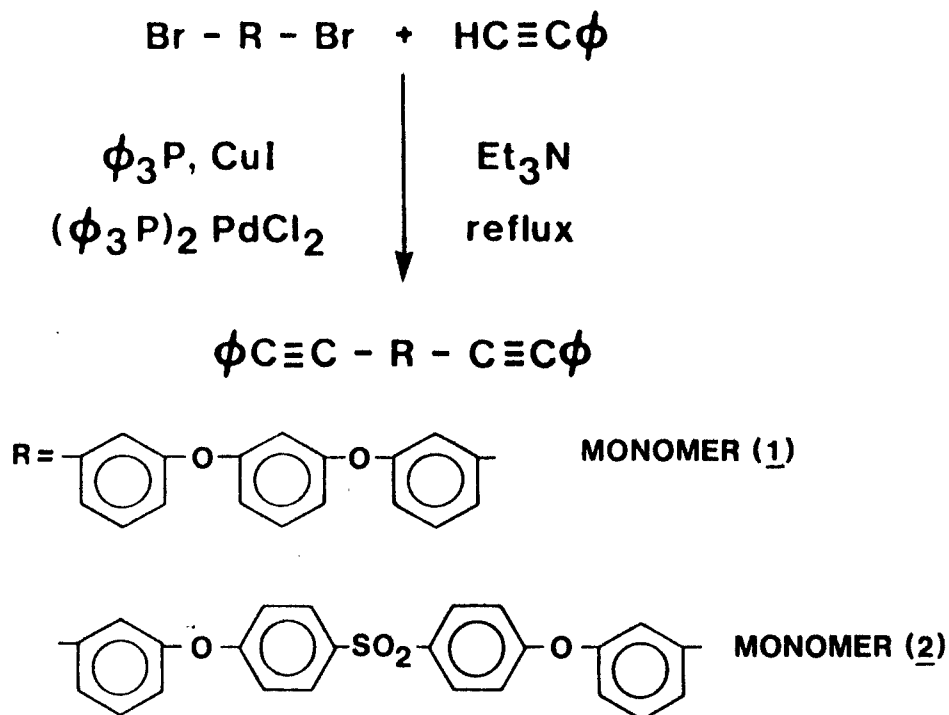
b. Ethynyl and Phenylethynyl Substituted Bisimides **3** and **4**.

The primary acetylene substituted bisimide **3** was prepared from the previously reported procedure (Reference 11) using the acetic acid catalysed condensation of 3-ethynylbenzenamine with 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidine] bis-1,3-isobenzofurandione (References 12 and 13).

MONOMER (**3**)
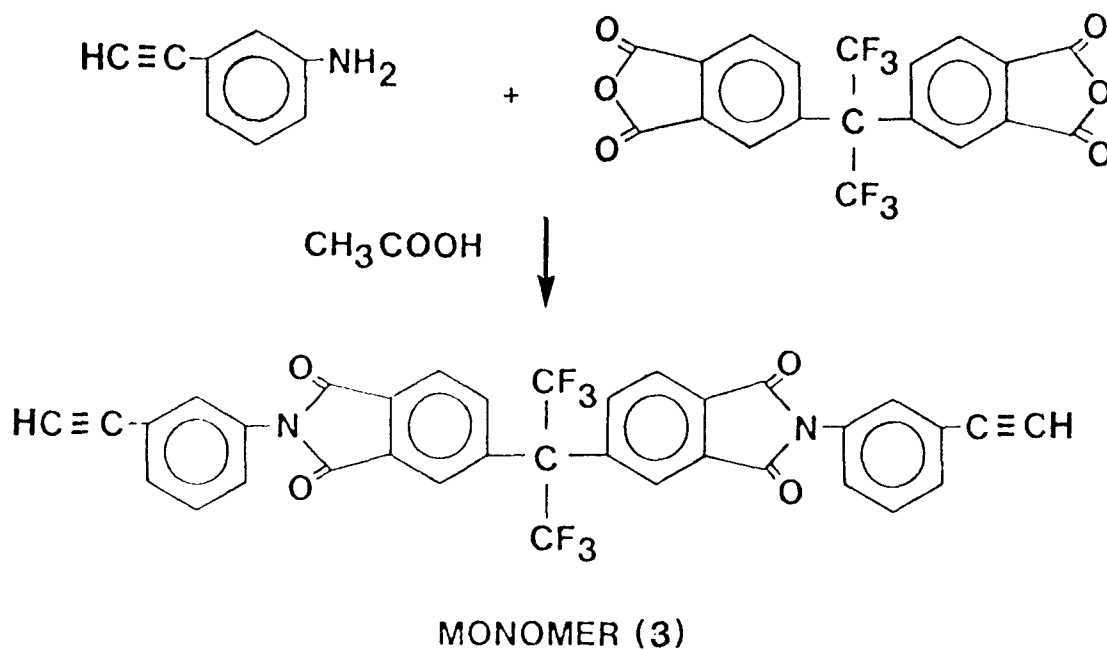
The phenylethynyl bisimide **4** was prepared in low yield by the same route (Reference 11) using 3-(phenylethynyl)-benzenamine (**5**) as the source of the secondary acetylene endcap. Compound **5** was prepared in 27% yield by chemical reduction with sodium hydrosulfite (Reference 14) of

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1-(phenylethynyl)-3-nitrobenzene (**6**). Compound **6** was prepared by a modification of a reported procedure (Reference 15) from cuprous phenylacetylide and 1-iodo-3-nitrobenzene.

$$\phi C \equiv CCu \ + \ I-\text{\textcircled{}}-NO_2 \ \xrightarrow{PYR} \ \phi C \equiv C-\text{\textcircled{}}-NO_2 \quad (\underline{6})$$

$$\downarrow \ \substack{Na_2S_2O_3 \\ THF/EtOH}$$

$$\phi C \equiv C-\text{\textcircled{}}-NH_2 \quad (\underline{5})$$

CH$_3$COOH
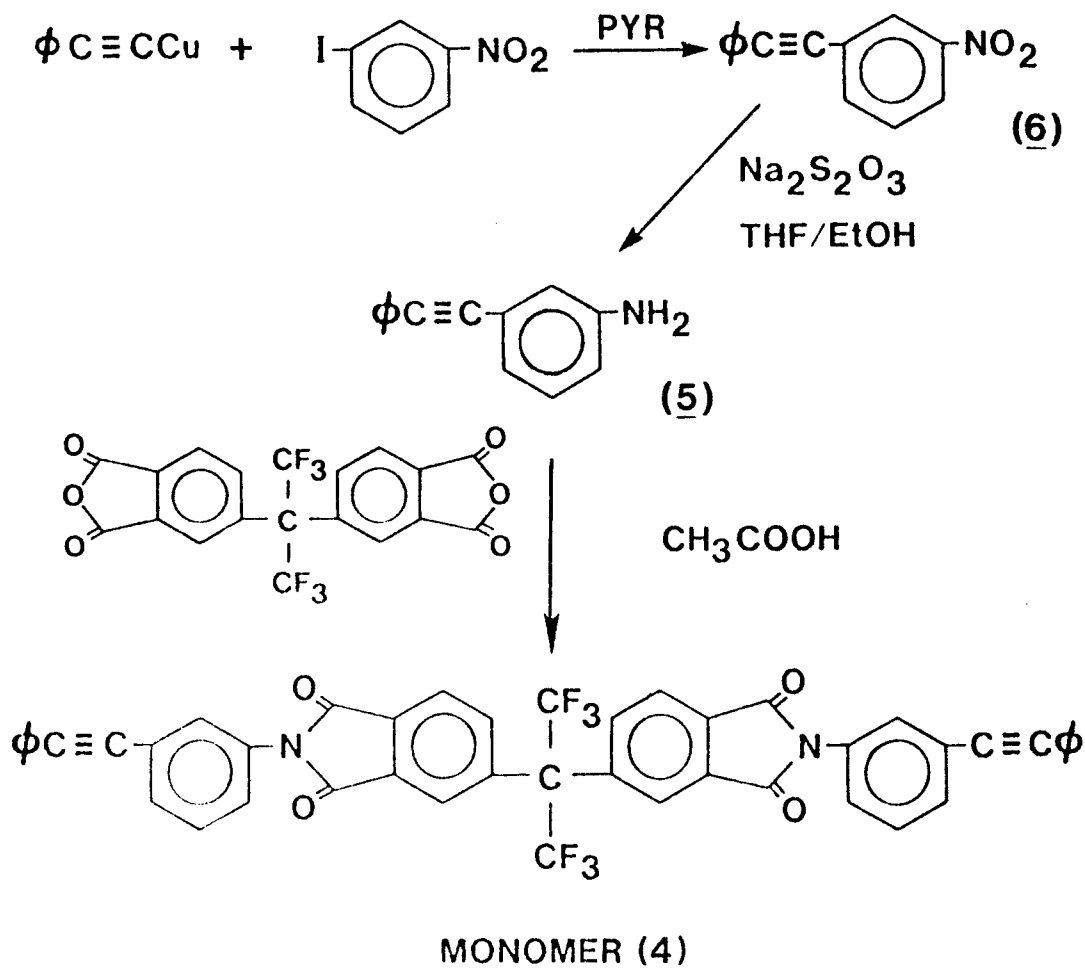
MONOMER (**4**)

2. Syntheses of Aryloxyethynyl Substituted Monomers with Phenylene R and Quinoxaline Moities in the Backbone

a. Aryloxyethynyl Phenylene R Monomers **7** and **8**

Monomers **7** and **8** were prepared in fair yield by the nucleophilic displacement reaction previously cited

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(Reference 10) with 1-phenoxy-3-(3-ethynylphenoxy)benzene (mono-ATP) (Reference 16) upon 2,2-bis[(3-bromophenoxy)-4-phenyl]propane (Reference 17) and 2,2-bis[(3-bromophenoxy)-4-phenyl]hexafluoropropane (Reference 9) respectively.
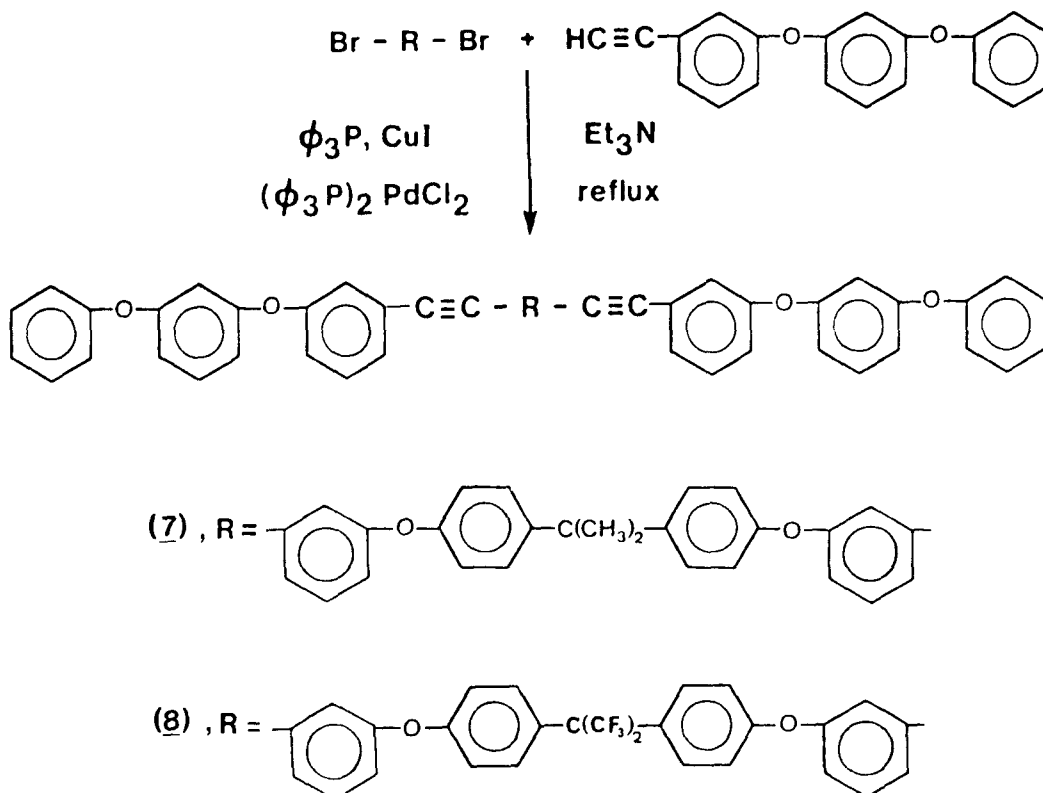
b. Aryloxyethynyl Biquinoxaline Monomers 9-12

Biquinoxaline monomers 9-12 were prepared in fair yields by the acetic acid catalysed condensation (Reference 18) of two moles of the appropriate phenoxyethynyl benzil 13 or 14 with one mole of either 3,3'-diaminobenzidine (DAB) or 3,3',4,4'-tetraaminodiphenyl ether (TADE). The benzils were prepared from a nucleophilic displacement

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reaction (Reference 10) using mono-ATP or 1-phenylsul-
fonyl-3-(3-ethynylphenoxy)benzene (mono-ATS) (Reference 19)
and 4-(3-bromophenoxy)benzil. 4-(3-Bromophenoxy)benzil was
prepared by a nitro displacement reaction using
4-nitrobenzil and 3-bromophenol (Reference 20).

$R'-C\equiv CH$ + Br——O——...

$R'-C\equiv C$——...

R=——(DAB)
R= 0 (TADE)

(13), R'=ϕOϕOϕ
(14), R'=-ϕOϕSO$_2\phi$

(9) =(13) + DAB
(10) =(13) + TADE
(11) =(14) + DAB
(12) =(14) + TADE
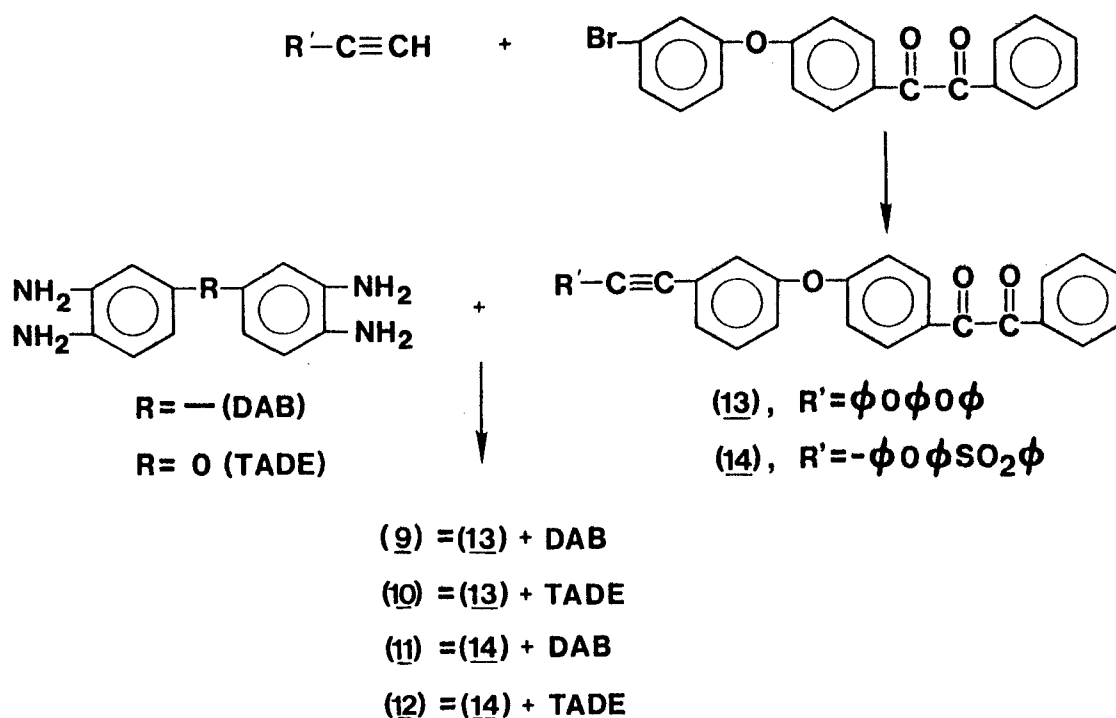
In the preparation of benzils 13 and 14 the Glaser
coupled products, formed from the coupling of the mono-ATP
or mono-ATS to itself in the presence of cuprous cations,
were removed by column chromatography at either this step
or at the final preparation of the biquinoxaline. It was
more advantageous to remove the coupled impurity at the
final monomer preparation when benzil 13 was used since
there was a larger difference in adsorbance on silica gel
between the biquinoxaline and the Glaser coupled mono-ATP

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than between benzil 13 and Glaser coupled mono-ATP.

3. Thermal and Thermomechanical Properties

The comparison of cured monomers 1 and 2 (Table 1) with the analogous AT system (Reference 9) by isothermal aging at 600°F is demonstrated in Figure 1. The final percentages of weight retained of 1 and 2 after isothermal aging for 200 hours in air versus the respective AT system were 72% to 24% for the phenylenes and 82% to 46% for the sulfones. With this encouraging data a series of monomers were prepared with both backbones of varied flexibility and thermooxidative stability and phenylethynyl terminations of varied flexibility.

To test the thermooxidative stability of the terminal phenylethynyl group, bisimide 4 was synthesized and compared to its AT analog, monomer 3. The backbone contained in 3 and 4 is known to possess sufficient thermooxidative stability to withstand long term exposure to a 350°C cure without degradation. Samples of 3 and 4 were cured under the conditions specified in Table 2. Isothermal aging of these samples at 600°, 650°, and 700°F for 200 hours in air (50 mL/min) (Figure 2) indicated a reversal in the trend observed in Figure 1; that is, the AT imide 3 was more thermooxidatively stable than the secondary substituted acetylene monomer 4 especially at temperatures above 600°F.

This observed reversal in stability may be explained by a thermally degradative process rather than a thermo-

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TABLE 1. Summary of Monomers for $R\left(\!-\!\bigcirc\!-\!C\equiv C-R'\right)_2$

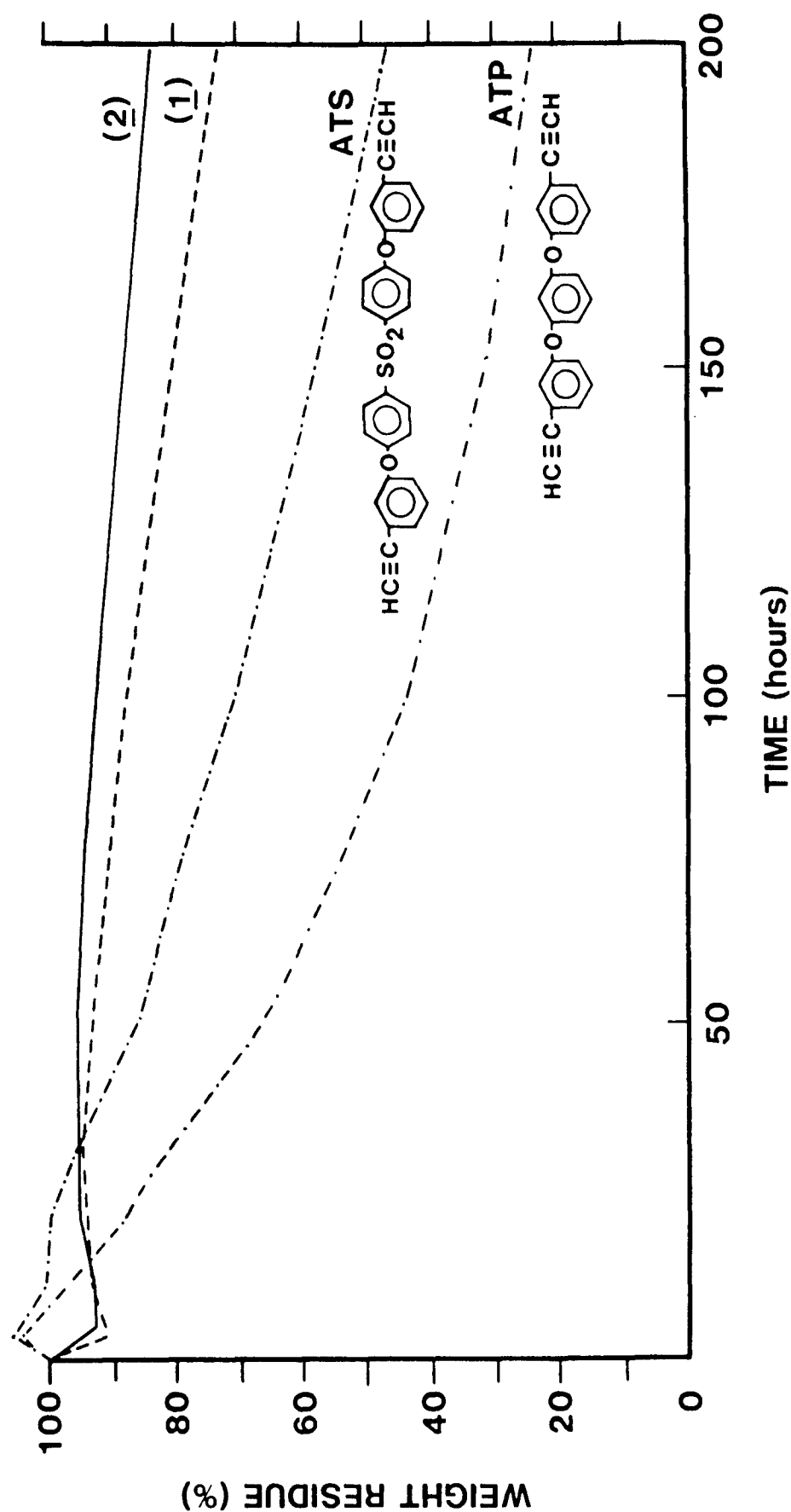| Monomers	R	R'
(1)	$-O-\bigcirc-O-$	$\bigcirc$
(2)	$-O-\bigcirc-SO_2-\bigcirc-O-$	$\bigcirc$
(3)	(dianhydride-imide with $C(CF_3)_2$ bridge)	H
(4)	(dianhydride-imide with $C(CF_3)_2$ bridge)	$\bigcirc$
(7)	$-O-\bigcirc-C(CH_3)_2-\bigcirc-O-$	$\bigcirc-O-\bigcirc-O-\bigcirc$
(8)	$-O-\bigcirc-C(CF_3)_2-\bigcirc-O-$	$\bigcirc-O-\bigcirc-O-\bigcirc$
(9)	(bis-quinoxaline, $-O-$ phenyl ends)	$\bigcirc-O-\bigcirc-O-\bigcirc$
(10)	(bis-quinoxaline ether, $-O-$ phenyl ends)	$\bigcirc-O-\bigcirc-O-\bigcirc$
(11)	(bis-quinoxaline, $-O-$ phenyl ends)	$\bigcirc-O-\bigcirc-SO_2-\bigcirc$
(12)	(bis-quinoxaline ether, $-O-$ phenyl ends)	$\bigcirc-O-\bigcirc-SO_2-\bigcirc$

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Figure 1. Isothermal Aging (600°F) of Monomers (1) and (2) Versus
Acetylene Terminated Phenylene R Systems.

TABLE 2. Yields and Thermal Characteristics of Monomers of Table 1.

Monomer	Yield (%)	T_g (°C)	T_{poly} (onset, °C)	T_{poly} (peak, °C)	T_g (cured, °C)	ITA (Air) (%)[a]
(1)	60	-1	280	379	246[b]	76
(2)	64	35	265	375	248[b]	82
(3)	73[c]	104[d]	132	182	–	94[e]
(4)	20	111	305	370	358[e]	92
(7)	40	48	225	392	99[f]	64
(8)	68	16	280	392	127[g]	84
(9)	38	75	346	400	193[h]	74
(10)	34	72	333	405	159[h]	80
(11)	59	124	353	399	242[h]	83
(12)	50	122	350	402	223[j]	78

[a] Weight residue after 200 hours at 600°F.
[b] Cure conditions: 250°C (482°F), nitrogen, 96 h.
[c] Reference 11.
[d] $T_m = 209$°C, T_{poly}(peak) = 219°C; value after recycle.
[e] Cure conditions: 350°C (662°F), nitrogen, 8 h.
[f] Cure conditions: 312°C (594°F), nitrogen, 8 h.
[g] Cure conditions: 312°C, nitrogen, 16 h.
[h] Cure conditions: 312°C, nitrogen, 24 h.
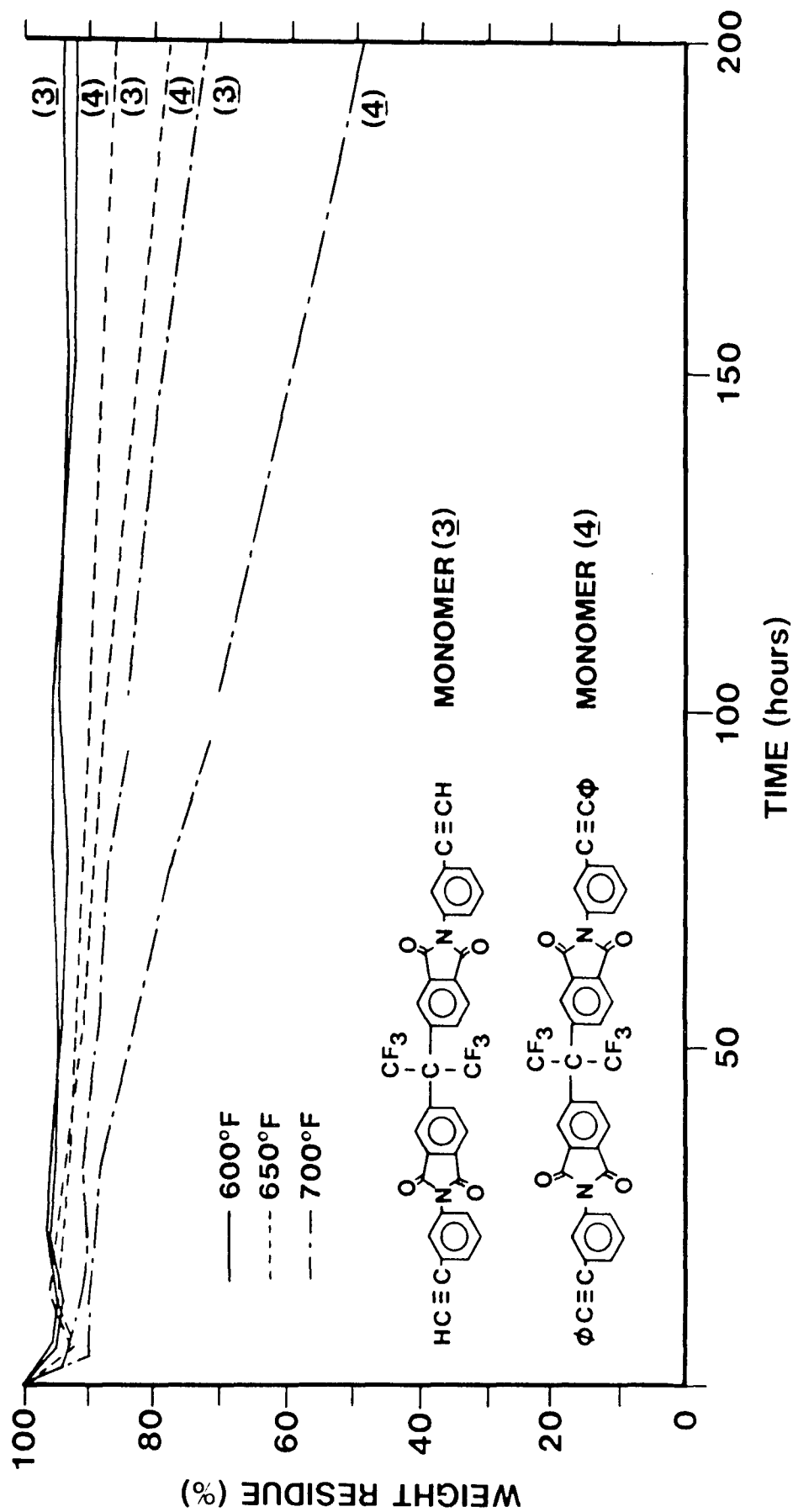[j] Cure conditions: 312°C, nitrogen, 48 h.

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Figure 2. Isothermal Aging of Monomers (3) and (4) at 600°, 650°, 700°F.

oxidative mechanism. At lower temperature (600°F), the pendant phenyl group shields the polyene cure site from a thermooxidative degradation. However, at the higher temperatures (650°-700°F), the phenyl pendant is thermally decomposed with the evolution of benzene resulting in substantial weight loss to the system. Mass spectrum-thermogravimetric analysis conducted under vacuum of cured specimens of monomer 4 indicated that degradation was initiated with the evolution of benzene at 400°C (Figure 3).

The final yields and thermoanalytical data for the phenylene R and biquinoxaline monomers with varying flexibility of the terminal secondary acetylene are summarized in Table 2. In general, the cure exotherms (T_{poly}) of the monomers exhibit typical Gaussian behavior with discernable cure onsets and maxima (DSC, $\Delta T = 20°C/min$) (Table 2). The exotherm maxima for biquinoxaline monomers 9-12 were approximately 400°C and varied from 370°-390°C for the phenylene R backbones in monomers 1, 2, 7, and 8, and the imide monomer 4. Within groups with similar endcaps the predictable trends in T_z with variation in the backbone are also apparent. The effect of the terminating phenylethynyl group on initial T_z is strongly demonstrated in monomers 9-12. The more rigid sulfone in the termini of 11 and 12 increases the initial T_z when compared to the corresponding phenoxy monomers 9 and 10 by approximately
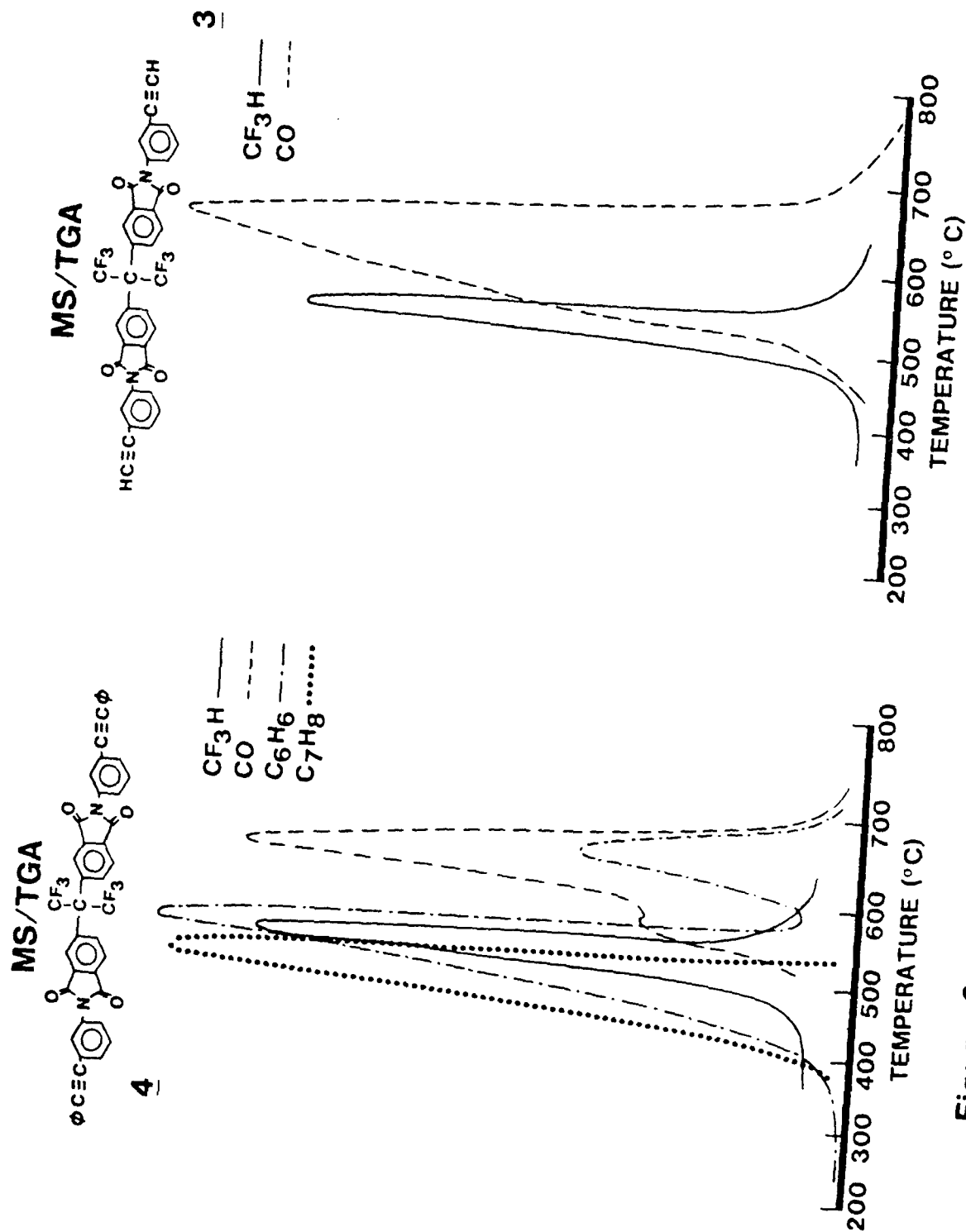
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Figure 3. Mass Spectrum–Thermogravimetric Analyses of Monomers (3) and (4).

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50°C. Finally, the effect of the ether linkage in the
backbones of cured specimens of monomers 10 and 12 is
demonstrated by the lowering of the T_g(cured) by 19°-34°C
when compared to biquinoxalines 9 and 11 respectively.

On an observational basis, monomer 9 appears to be more
thermooxidatively stable than its AT counterpart, BA-DAB-BA
(Reference 18). Cured specimens of 9 do not swell upon
exposure to N,N-dimethylformamide at room temperature for
one week. Similar exposure to methylene chloride produces
only slight swelling. Visual examination of a cured sample
of 9 indicates that a less brittle, more lightly
crosslinked product is achieved when compared to previously
prepared resins containing primary acetylenic termini.

In general, the lower T_g's (cured) exhibited by the
monomers with the bulky aryloxy groups indicate that the
systems are substantially less crosslinked. The T_g's
(cured) are more representative of a linear polymeric
backbone such as polystyrene. Based on a theoretical T_g
calculation (Reference 21) the predicted T_g(cured) of 9 for
the completely linear homopolymer is 185°C. The
experimentally measured T_g(cured) of 193°C for 9 thus
correlates closely with the value predicted for the purely
linear system.

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To test the possible improvement in thermomechanical properties a fracture study on a cured specimen of $\underline{9}$ was performed and the observed K_Q at room temperature was 0.78 $\pm$ 0.03 MPa versus the reported K_Q of BA-DAB-BA of 0.65 $\pm$ 0.7 MPa (Reference 22). This K_Q measurement of $\underline{9}$ represents a 20% improvement in the toughness of the cured biquinoxaline when secondary acetylene end groups are utilized.

SECTION III

EXPERIMENTAL

All amine solvents, commercially available, were distilled and stored over molecular sieves (Linde 4A) before use. All other solvents and reagents were used without further purification. Melting points were uncorrected. Fracture analysis was performed on a Mechanical Testing System Model 773 at room temperature with a load rate of 0.02 inches/min. Thermal analytical work was performed on a DuPont 910 DSC apparatus with Omnitherm 35053 three-module controller ($\Delta T=20^{\circ}C/min$). Electron impact mass spectrum (E.I.M.S) was performed on a Finnigan GC/MS/DS system Model 4021. Infrared spectra were performed on a Beckman IR-33. Proton N.M.R. spectra were recorded on a Varian EM 360A spectrophotometer.

1,3-Bis(3-phenylethynylphenoxy)benzene (1):

A solution of 1,3-bis(3-bromophenoxy)benzene (Reference 10) (6.24g, 14.85 mmol) and phenylacetylene (3.27g, 32.02 mmol) in triethylamine (80 mL) was degassed by bubbling nitrogen gas through the mixture for 20 min at room temperature. To the degassed mixture was added bis(triphenylphosphine)palladium dichloride (0.03g, 0.04 mmol), triphenylphosphine (0.30g, 1.14 mmol) and cuprous iodide (0.12g, 0.62 mmol). The reaction mixture

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was then heated at reflux under nitrogen for 16h. The reaction mixture was cooled to room temperature and filtered to remove precipitated triethylamine hydrobromide. The triethylamine filtrate was concentrated under reduced pressure to give an oil. The crude oily product was purified by column chromatography on silica gel using hexane as the eluent. Concentration of the hexane solution containing the third band from the column gave a white crystalline solid: 4.20g, (60%); m.p. 78-79°C.

$C_{34}H_{22}O_2$ calc.   C 88.29   H 4.79

(462.52)   found   88.58   4.91

4,4'-Bis(3-phenylethynylphenoxy)diphenyl sulfone (2):

The reaction of 4,4'-bis(3-bromophenoxy)diphenyl sulfone (Reference 10) (4.00g, 7.11 mmol) with phenylacetylene (1.64g, 16.06 mmol) was catalyzed by bis(triphenylphosphine)palladium dichloride (0.03g, 0.04 mmol), triphenylphosphine (0.30g, 1.14 mmol) and cuprous iodide (0.12g, 0.62 mmol) using the procedure described above to give a crude oily product. The oil was purified by

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column chromatography on silica gel using 3:1 hexane:
methylene chloride as the eluent to give a solid:
2.75g (64%); m.p. 55-56°C.

$C_{40}H_{26}O_4S$ calc. C 79.71 H 4.35 S 5.32

(602.67)   79.91   4.40   5.14

5,5'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-(1-(3-ethynyl)phenyl)-1H-isoindole-(2H)-dione (3):

Monomer 3 was prepared in 27% yield according to the
literature procedure (Reference 11) by the acetic acid
catalyzed condensation of 3-ethynylbenzenamine (2 mol) with
5,5'-[2,2,2-trifluoromethyl)ethylidene]bis-1,3-isobenzo-
furandione (1 mol) (References 12 and 13).

5,5'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-(1-(3-phenylethynyl)phenyl)-1H-isoindole-(2H)-dione(4):

A solution of 5,5'-[2,2,2-trifluoromethyl)ethylidene]
bis-1,3-isobenzofurandione (4.52g, 10.19 mmol), benzenamine
5 (5.90g, 30.57 mmol) and glacial acetic acid (100 mL) was
stirred at room temperature under a nitrogen atmosphere for
0.5h before the flask was heated to an internal temperature

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of 80°C. After stirring for 3h at 80°C the flask was heated to reflux (115°C) for 2h. TLC on an activated silica gel strip (2:1 diethyl ether:hexane; diethyl ether) indicated full closure to bisimide 4. The solution was allowed to cool to room temperature and the crude product was afforded by precipitation of the acidic solution into water (500 mL). The precipitate was dissolved into methylene chloride (100 mL) and washed with 10% sodium bicarbonate (2 X 100 mL), water (2 X 100 mL), and dried over anhydrous magnesium sulfate (5.00g). The solvent was distilled by rotary evaporation to afford a light beige solid (27.90g). The pure product was isolated by column chromatography on silica gel (Woelm DCC, 2.5 cm dia X 39 cm L) using chloroform as the eluent. Precipitation from chloroform:methanol (25 mL:100 mL) and subsequent drying in a 60°C oven at reduced pressure afforded a white powder: 1.52g (20%).

$C_{47}H_{24}F_6N_2O_4$ calc. C 71.03 H 3.02 N 3.53

(794.68)   found   70.92   3.34   3.54

I.R. (KBr): v=3080, 2200, 1790, 1730, 1630, 1600, 1580 cm^{-1} (Figure 4).

3-(Phenylethynyl)benzenamine (5):
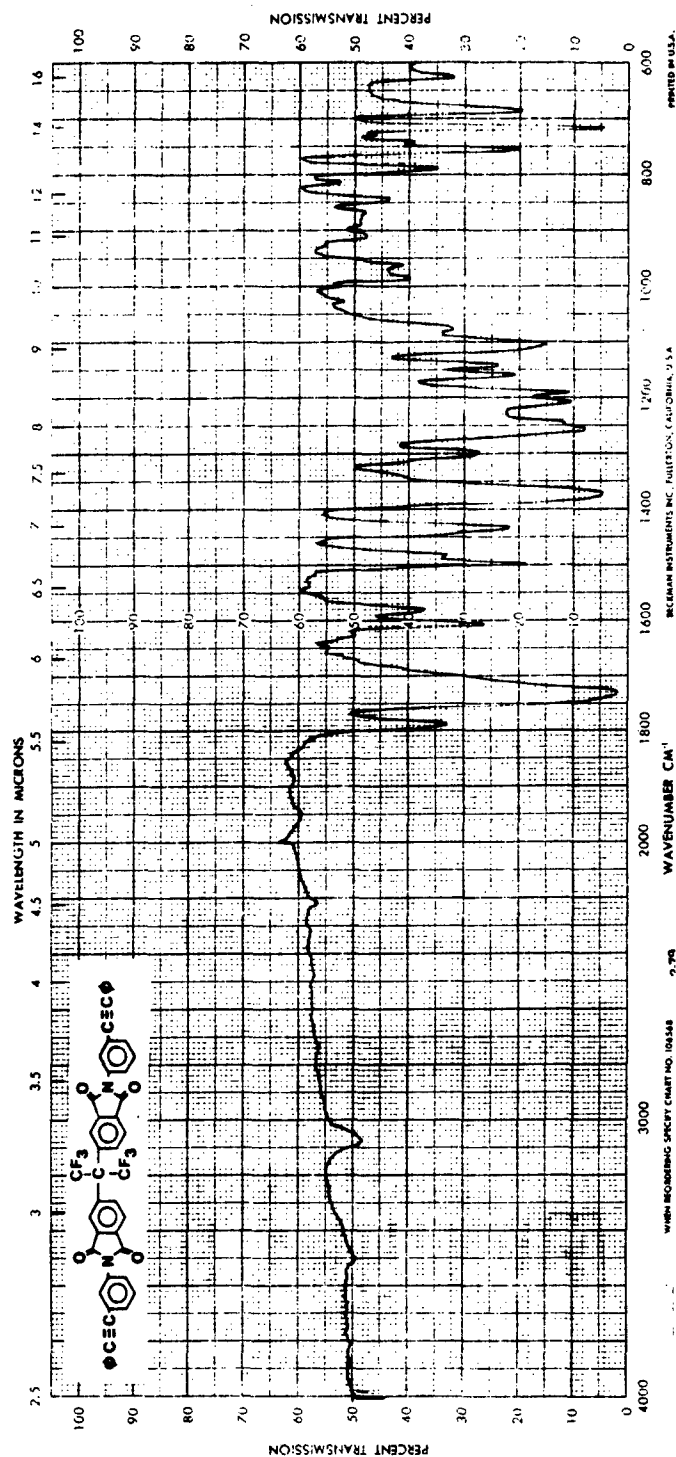
To a degassed solution of 6 (18.51g, 82.92 mmol) in

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Figure 4. IR Spectrum of Monomer 4.

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tetrahydrofuran:ethanol (25 mL:500 mL) was dropwise added a solution of sodium hydrosulfite (57.77g, 331.82 mmol) in water (500 mL) over a period of 15 min. After stirring at room temperature for 5 min TLC of the reaction on a silica gel strip (4:1 hexane:diethyl ether; diethyl ether) indicated the reaction was complete. The solution was extracted with methylene chloride (3 X 250 mL) and the organic layers were washed with water (3 X 500 mL) and dried over anhydrous magnesium sulfate (20.00g). Distillation of the solvent in vacuo afforded a golden yellow oil. The oil was dissolved in boiling methylene chloride: hexane (25 mL:150 mL) and the hot solution was decanted from the tarry residue to afford a brown solid: 4.72g (27%); m.p. 43-44°C [Reference 23, m.p. 46.5-47.5°C].

^{1}H-N.M.R. (CDCl$_3$/TMS$_{int}$, 60 MHz): δ=7.7-6.6 (m, 9H$_{arom}$), 3.6 (s, 2H$_{amine}$) (Figure 5).

I.R. (KBr): ν=3480, 3400, 3080, 2200, 1620, 1600, 1580, 1250 cm^{-1} (Figure 6).

E.I.M.S. [70 eV]: m/z=193 (M$^+$, 100).

1-(Phenylethynyl)-3-nitrobenzene (6):

A solution of 1-iodo-3-nitrobenzene (32.37g, 130.00 mmol) and pyridine (250ml) was degassed at room temperature under nitrogen before the addition of cuprous phenylacetylide (Reference 14) (21.41g, 130.00 mmol). The solution

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Figure 5. ¹H NMR Spectrum of Compound 5.
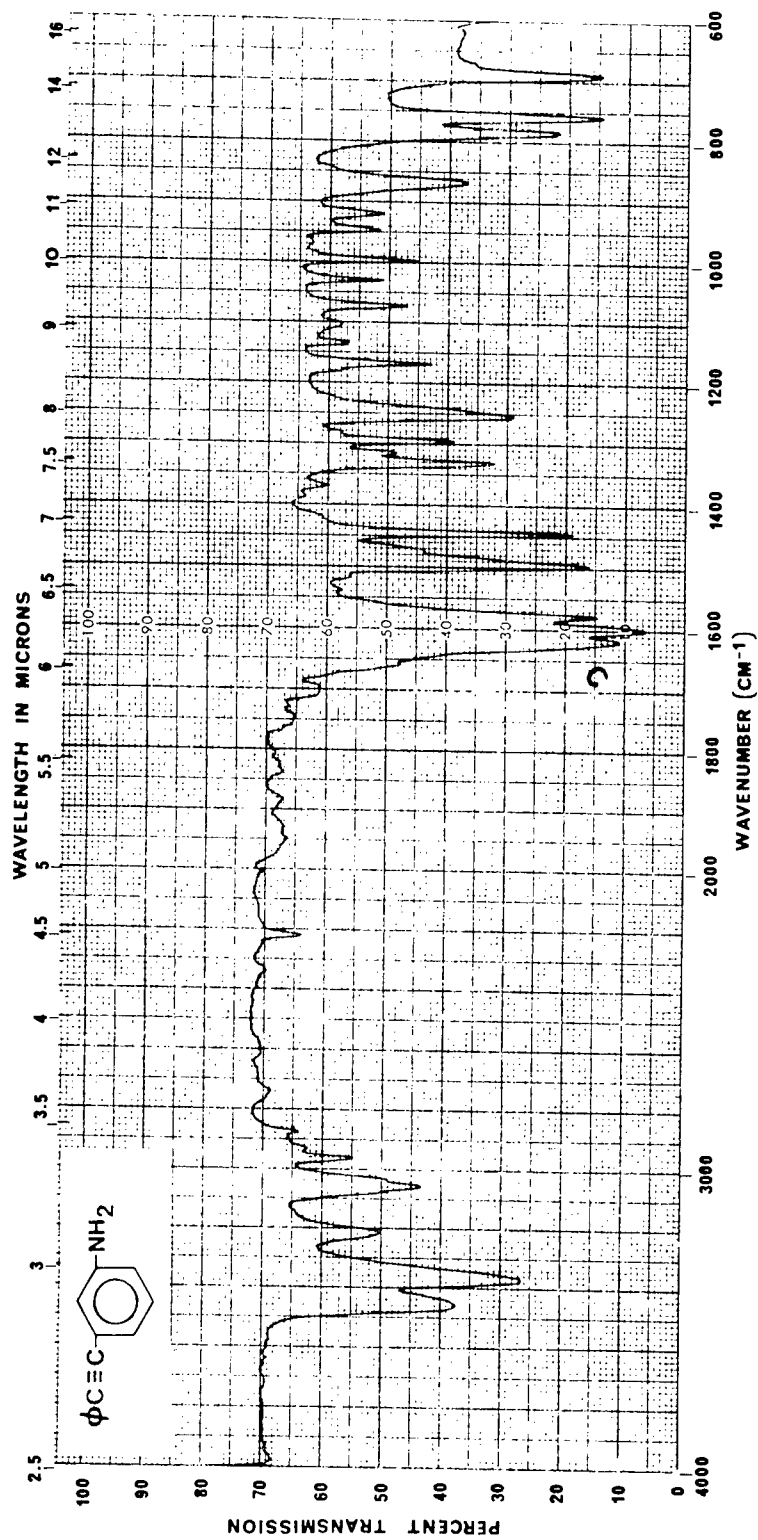
φC≡C—⟨benzene ring⟩—NH₂
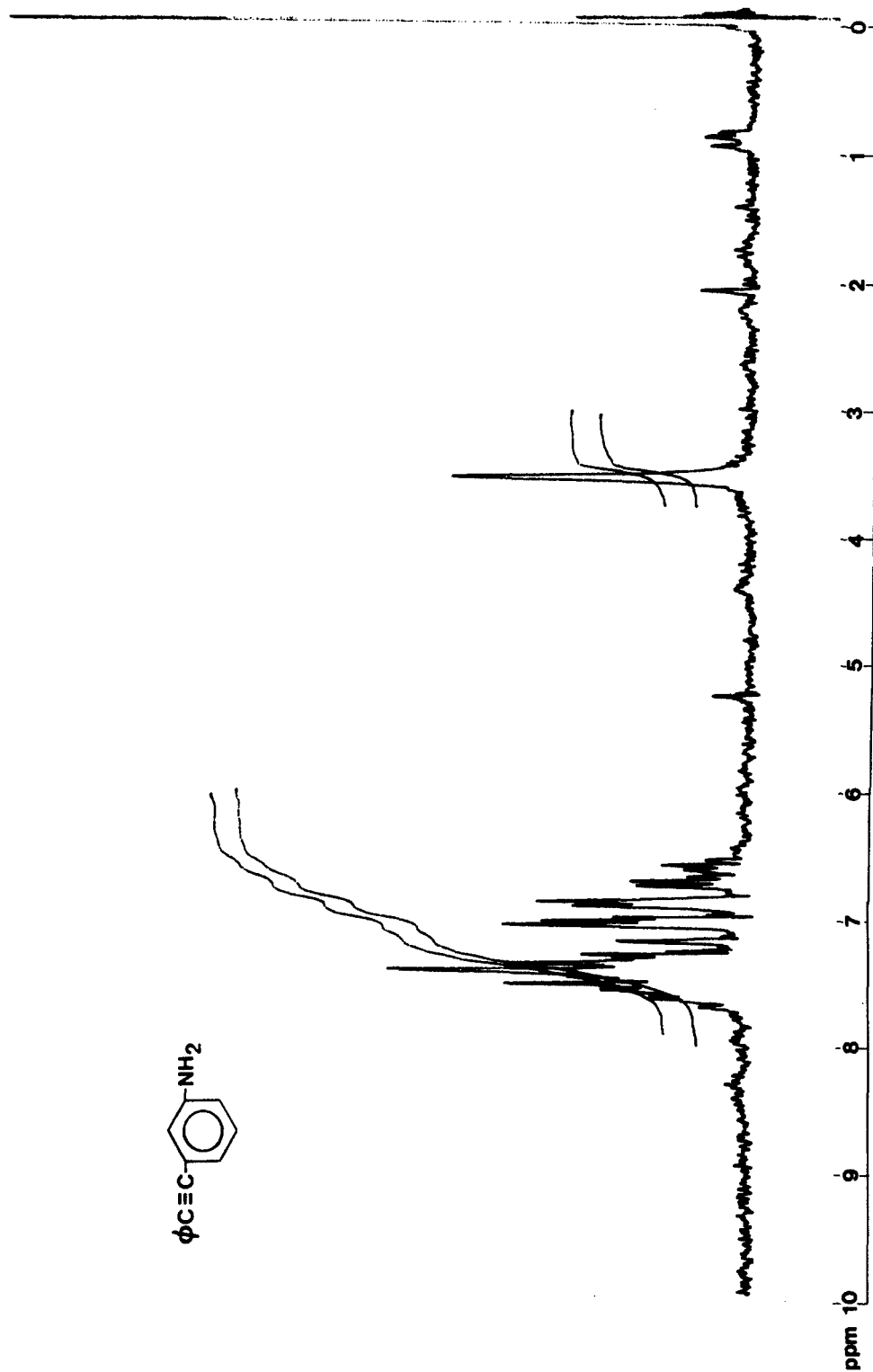
Figure 6. IR Spectrum of Compound 5.

was heated to reflux (115°C) under a nitrogen atmosphere for 5h until TLC on an activated silica gel strip (4:1 hexane: methylene chloride) indicated the reaction was complete. The solvent was distilled under vacuum and the residue was dissolved in methylene chloride (250 mL). The organic solution was filtered over diatomaceous earth (2.5 cm H) to remove the pyridinium iodide salts. The filtrate was washed with 10% sulfuric acid (700 mL), 15% hydrochloric acid (3 X 150 mL), and water (3 X 300 mL). After drying over anhydrous magnesium sulfate (12.00g) the solvent was distilled by rotary evaporation to give a brown solid (26.18g). The crude product was recrystallized from ethanol with decolorizing carbon to give pale yellow needles: 19.55g (67%); m.p. 64-66°C.

$C_{14}H_9NO_2$ calc. C 75.32 H 4.06 N 6.28

(223.22) found 75.40 3.99 6.00

^{1}H-N.M.R. (CDCl$_3$/TMS$_{int}$, 60 MHz): δ=8.4-7.3 ppm (9H$_{arom}$) (Figure 7).

I.R. (KBr): ν=3080, 2200, 1600, 1510, 1340 cm^{-1} (Figure 8).
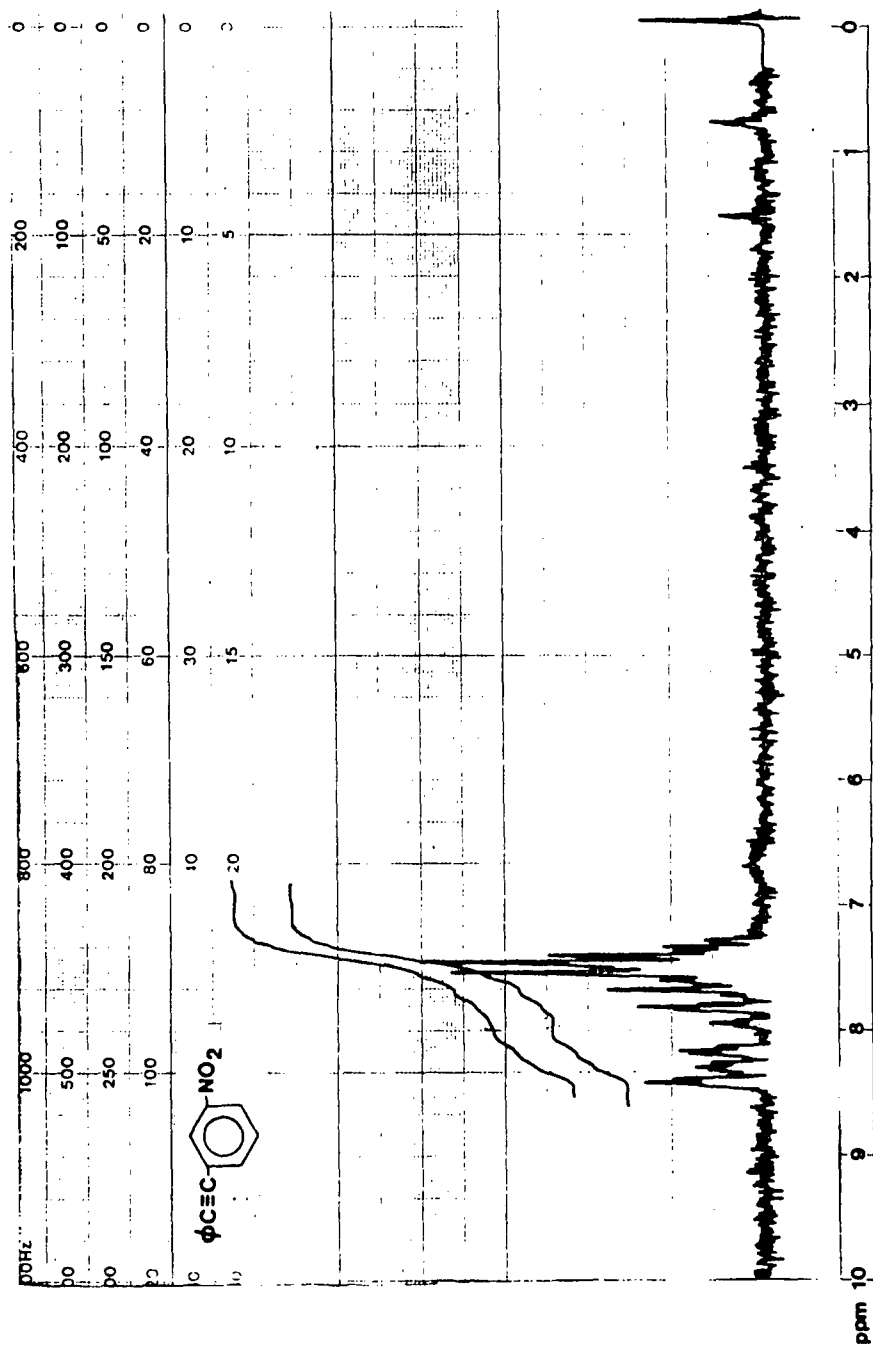
E.I.M.S. [70 eV]: m/z=223 (M$^+$, 100).

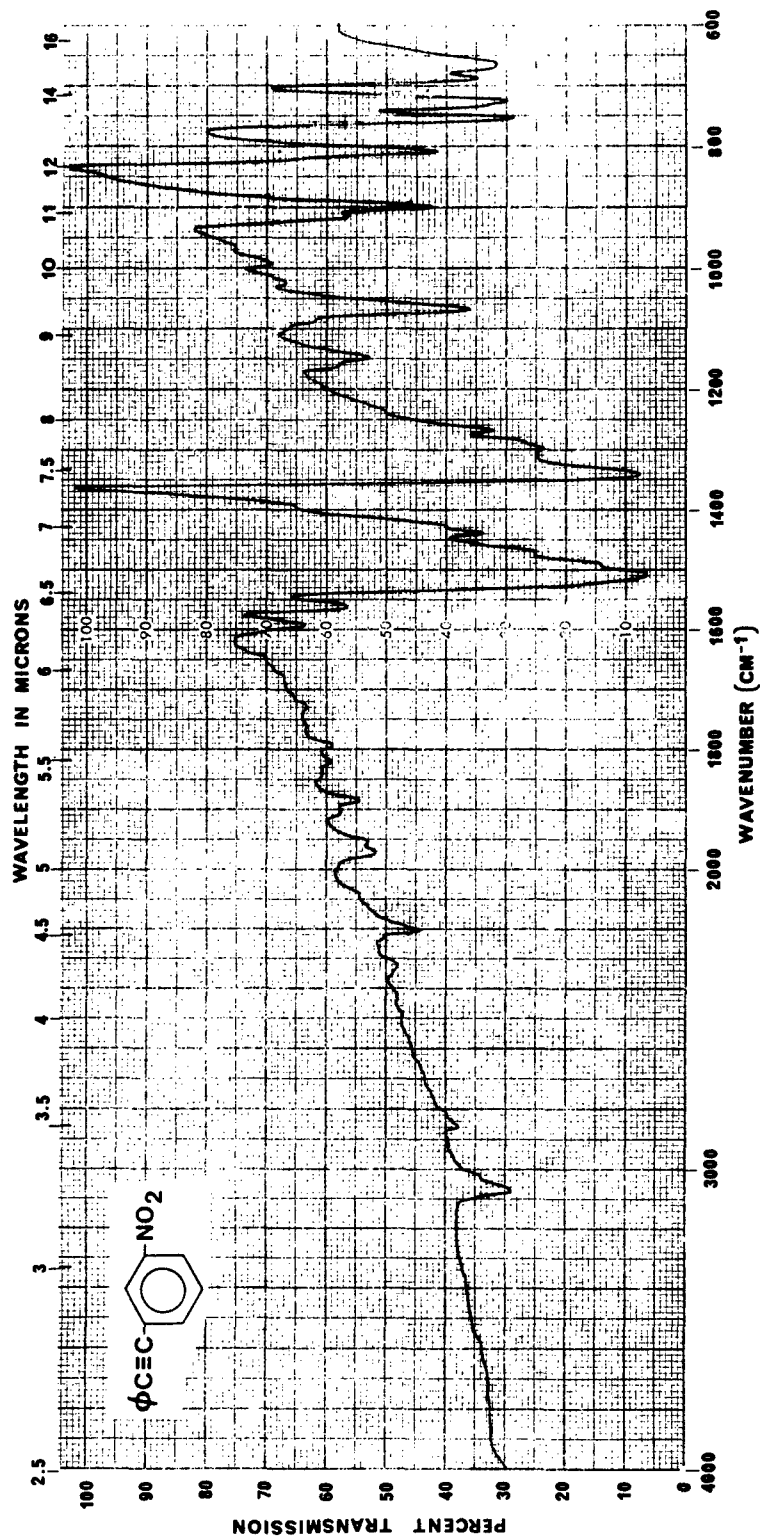Figure 7. ^{1}H NMR Spectrum of Compound 6.

Figure 8. IR Spectrum of Compound 8.

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1,1'-[2-propylidene]bis[4-[3-[[3-(3-phenoxyphenoxy)-phenyl]ethynyl]phenoxy]benzene (7):

A suspension of 2,2-bis[(3-bromophenoxy)-4-phenyl]-
propane (3.73g, 6.93 mmol) (Reference 17), mono-ATP (4.22g,
14.77 mmol) (Reference 16), triethylamine (distilled, 80
mL) and triphenylphosphine (0.20g, 0.76 mmol) were degassed
at room temperature under a nitrogen purge for 10 min
before the addition of cuprous iodide (0.12g, 0.62 mmol)
and bis(triphenylphosphine)palladium dichloride (0.03g,
0.04 mmol). The solution was heated at reflux under a
nitrogen atmosphere for 24h at which time TLC on an acti-
vated silica gel strip (2:1 hexane:diethyl ether) indicated
the reaction was complete. After the flask was allowed to
cool to room temperature the solution was filtered over
diatomaceous earth to remove the triethylamine hydrobromide
salts. The organic filtrate was washed with 15% hydro-
chloric acid (100 mL) and extracted with methylene chloride
(2 X 50 mL). The organic layers were washed with water (4
X 200 mL) and dried over anhydrous magnesium sulfate
(5.00g). The solvent was distilled by rotary evaporation
to give a dark brown oil (7.87g). Chromatography on a
silica gel column (Woelm DCC, 3 cm dia X 50 cm H) using 2:1

hexane:methylene chloride to remove the product resulted in a light yellow glass: 2.60g (40%).

$C_{67}H_{46}O_6$ calc. C 84.79 H 5.10

(949.05) found 84.86 5.16

Pd <2 ppm

^{1}H-N.M.R. (CDCl$_3$/TMS$_{int}$, 60 MHz): δ=7.4-6.7 (m, 42H$_{arom}$), 1.7 (s, 6H$_{methyl}$) (Figure 9).

E.I.M.S. [70 eV]: m/z=948 (M$^+$, 20), 44 (100).

1,1'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis-[4-[3-[[3-(3-phenoxyphenoxy)phenyl]ethynyl]phenoxy]benzene (8):

Monomer 8 was prepared by addition of 2,2-bis[(3-bromophenoxy)-4-phenyl]hexafluoropropane (4.91g, 7.60 mmol), mono-ATP (6.52g, 22.80 mmol), triethylamine (125 mL), triphenylphosphine (0.40g, 1.53 mmol), cuprous iodide (0.20g, 1.05 mmol), and bis(triphenylphosphine)palladium dichloride (0.20g, 0.29 mmol) in the order previously described for the preparation of monomer 7. The reaction was heated at 90°C under an inert atmosphere for 8h. After the neutralization washes as previously described, a brown solid was afforded (10.35g). Column chromatography on silica gel (3 cm dia X 75 cm H) using 4:1 hexane:carbon
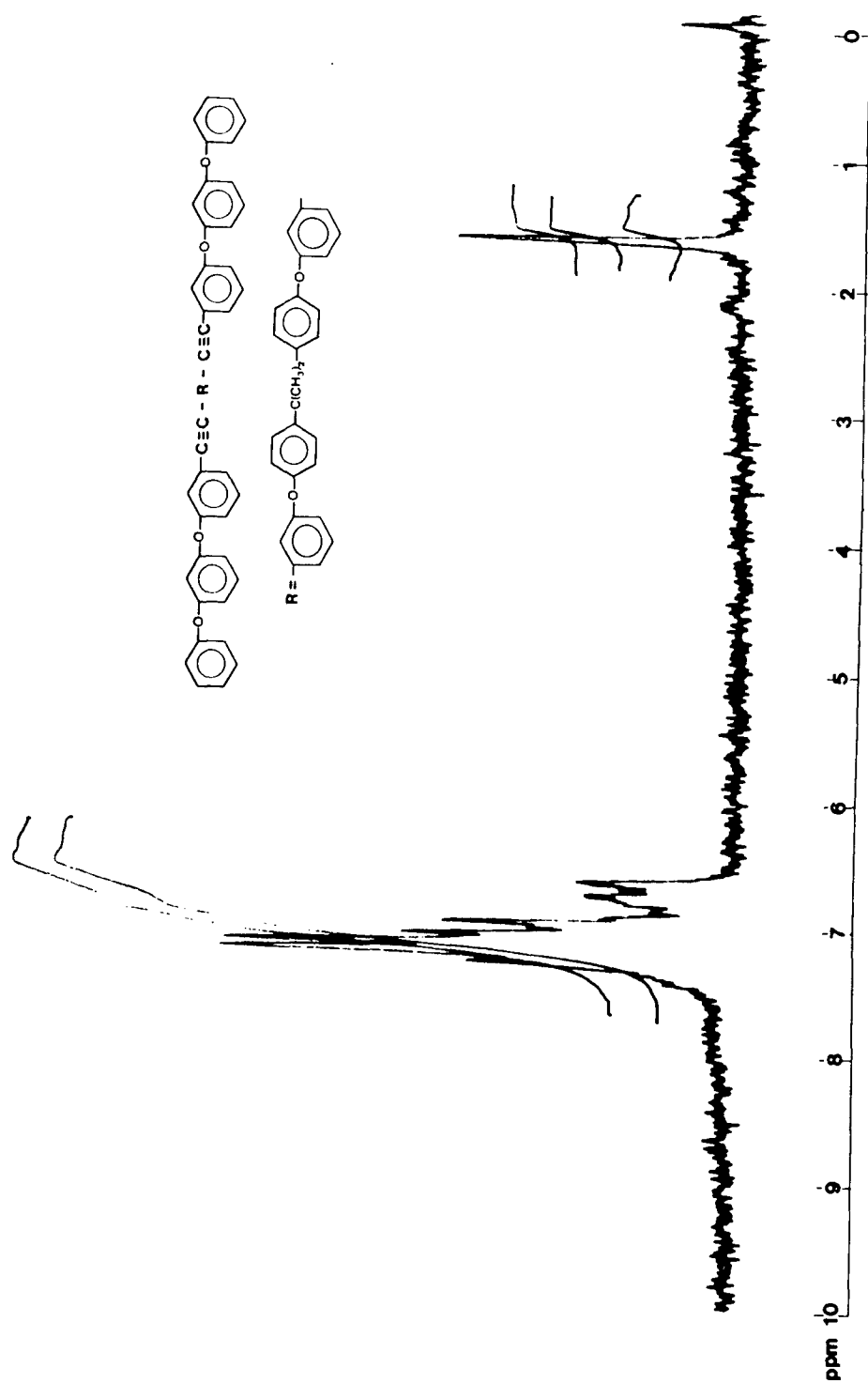
Figure 9. ^{1}H NMR Spectrum of Monomer $\underline{7}$.

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tetrachloride as the eluent afforded a light yellow powder:
5.47g (68%).

$C_{67}H_{42}Fe_6O_6$ calc.   C 76.13   H 4.00

(1056.98)   found   75.93   4.07

Biquinoxaline Monomers (9)-(12); Representative Procedure:

A solution of 13 (34.08g, 58.16 mmol) in tetrahydro-
furan (400 mL) was stirred at room temperature for 0.5h
under a nitrogen purge before the addition of DAB (6.22g,
29.07 mmol). After 0.3h additional stirring at room
temperature a catalytic quantity of glacial acetic acid (2
mL) was added and the solution was stirred at room
temperature for 18h or until TLC on an activated silica gel
strip (2:1 diethyl ether:hexane) indicated the absence of
benzil. The solution was poured into water (800 mL) and
the aqueous layer was extracted twice with methylene
chloride (2 X 200 mL). The organic layers were combined,
washed with 5% sodium bicarbonate (500 mL) and dried over
anhydrous magnesium sulfate (40.00g). Distillation of the
solvent by rotary evaporation afforded a dark brown oil
(71.46g). The oily residue was dissolved in 1:1 hexane:
methylene chloride (100 mL) and separated into four 25 mL
portions. Each portion was chromatographed on a silica gel
column (Woelm DCC, 354.19g, 5 cm dia X 37 cm H) using 2:1

hexane:methylene chloride to remove the unreactive Glaser coupled products and 2:1 methylene chloride:hexane to remove the product. The product fractions were distilled to dryness by rotary evaporation and the residue was precipitated three times from tetrahydrofuran:methanol (100/1500 mL) to afford 9 as a light yellow powder (Table 3 and Figure 10).

1-[4-[3-[[3-(3-Phenoxyphenoxy)phenyl]ethynyl]phenoxy]-phenyl]-2-phenylethane dione (13):

A solution of 4-(3-bromophenoxy)benzil (Reference 20) (11.08g, 29.08 mmol), mono-ATP (21.64g, 75.66 mmol), triethylamine (150 mL) and triphenylphosphine (0.40g, 1.53 mmol) was stirred at room temperature under a nitrogen purge for 0.5h before the addition of cuprous iodide (0.20g, 1.05 mmol) and bis(triphenylphosphine)palladium dichloride (0.20g, 0.29 mmol). The solution was heated to an internal temperature of 90°C under a nitrogen atmosphere until TLC on an activated silica gel strip (4:1 hexane: diethyl ether) indicated reaction completion (4h). The flask was allowed to cool to room temperature and the solution was neutralized with 15% hydrochloric acid (2 X 150 mL) and extracted with methylene chloride (100 mL). The organic layer was separated from the acidic solution,

TABLE 3

CHARACTERIZATION SUMMARY OF MONOMERS 9-12

Monomer	Appear-ance	Isolating Eluent	Elem. Anal.[a,b] Calc. (Found)		Cu (ppm)	Pd (ppm)
9	yellow pwd.	2:1 CH₂Cl₂: C₆H₁₄	C 84.00 (84.02) H 4.44 (4.63) N 4.26 (3.91)		14	<4
10	beige pwd.	2:1 CH₂Cl₂: C₆H₁₄	C 82.99 (82.88) H 4.39 (4.51) N 4.21 (3.83)		(c)	(c)
11	yellow pwd.	CH₂Cl₂	C 78.28 (78.12) H 4.14 (4.10) N 3.97 (4.00) S 4.54 (4.47)		(c)	(c)
12	white pwd.	CH₂Cl₂	C 77.40 (77.13) H 4.10 (4.20) N 3.92 (3.85) S 4.49 (4.33)		(c)	(c)

(a) Analyses for C, H, N performed on a Perkin-Elmer Elemental Analyser Model 240C.

(b) Analysis for S performed by a titration technique reported by Fritz and Freeland (Reference 24).
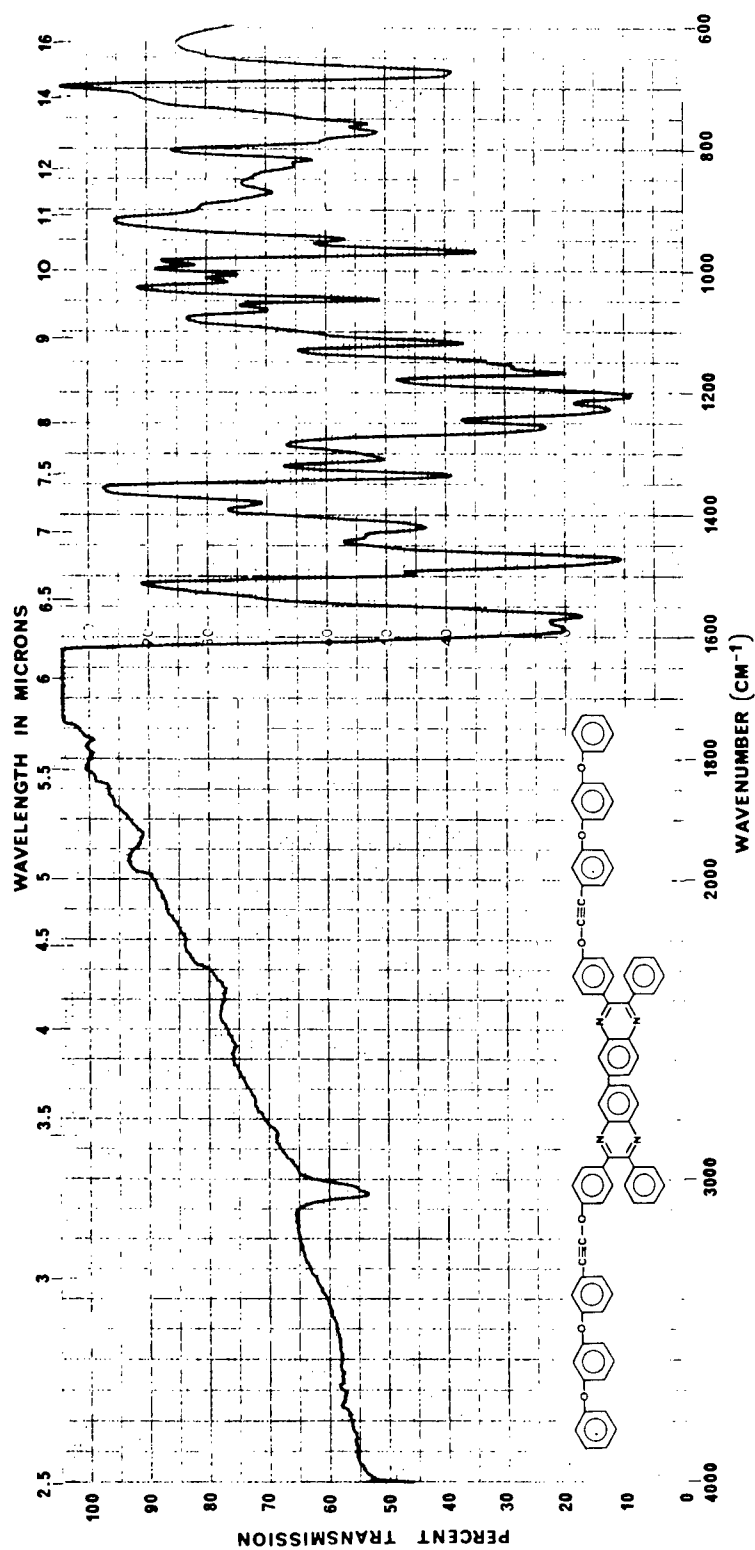
(c) Not available.

Figure 10. IR Spectrum of Monomer 9.

washed with water (3 X 500 mL) and dried over anhydrous magnesium sulfate (10.00g). Following a filtration over silica gel (Woelm DCC, 55.17g, 5 cm H) in a coarse porosity fritted Buchner funnel the filtrate was distilled to dryness by rotary evaporation and dried _in vacuo_ at 50°C for 8h to afford a brown tacky solid (30.24g). The product was used without further purification despite the presence of Glaser coupled products as contaminants.

1-[4-[3-[[3-(4-phenoxysulfonylphenoxy)phenyl]ethynyl]-phenoxy]phenyl]-2-phenylethanedione (14):

A solution of 4-(3-bromophenoxy)benzil (Reference 20) (0.80g, 2.36 mmol), 1-phenylsulfonyl-4-(3-ethynylphenoxy)-benzene (Reference 19) (2.38g, 6.26 mmol), triethylamine (50 mL), pyridine (10 mL), and triphenylphosphine (0.40g, 1.53 mmol) were stirred at room temperature under a nitrogen purge for 0.3h before the addition of cuprous iodide (0.20g, 1.05 mmol) and bis(triphenylphosphine)-palladium dichloride (0.20g, 0.29 mmol). The solution was heated to an internal temperature of 90°C under a nitrogen atmosphere until TLC on an activated silica gel strip (4:1 hexane:methylene chloride) indicated reaction completion (20h). The solution was allowed to cool to room temperature and was neutralized by pouring the solution into 15%

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hydrochloric acid (115 mL). After two extractions of the
aqueous solution with methylene chloride (2 X 50 mL) the
organic layers were combined, washed with water (2 X 100
mL) and dried over anhydrous magnesium sulfate (0.50g).
Distillation of the solvent by rotary evaporation afforded
a dark brown oil (4.39g) which was chromatographed on a
silica gel column (Woelm DCC, 3 cm dia X 32 cm H) using 2:1
hexane:methylene chloride to remove the Glaser coupled
products and methylene chloride to remove the product.
Distillation of the solvent afforded a yellow amorphous
solid: 1.25g (84%). .

$C_{40}H_{26}O_6S$ calc. C 75.69 H 4.13 S 5.05

(634.67)   found   74.68   4.36   5.03

I.R. (KBr): v=3090, 1600, 1580, 1330, 1250, 1160, 1010 cm^{-1}
(Figure 11).

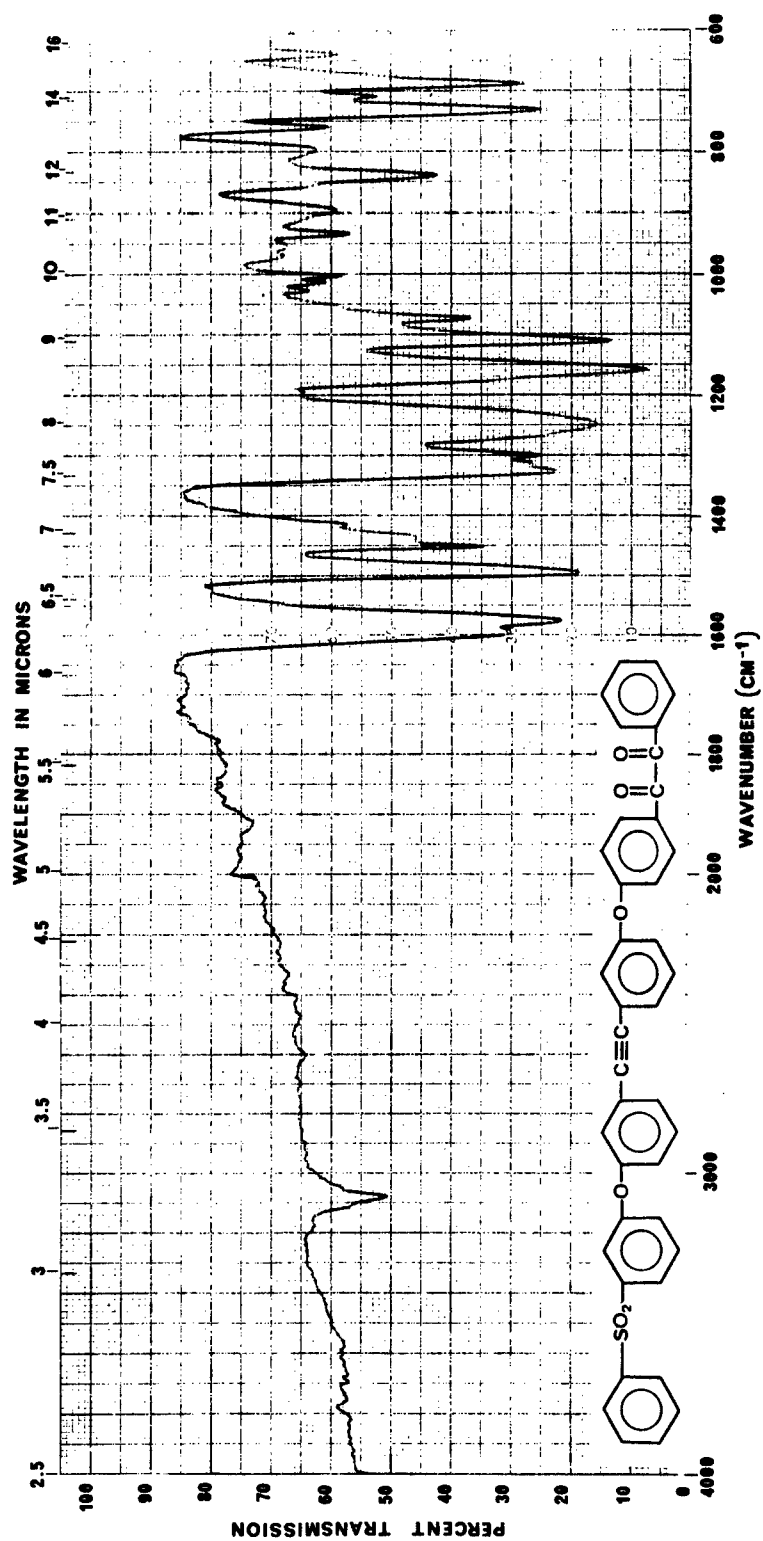E.I.M.S. [70eV]: m/z=634 (2, M^+), 105 (100).

Figure 11. IR Spectrum of Compound 14.

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